THE ELECTRIC MOMENTS OF ORGANIC PEROXIDES. III. PERESTERS[1]

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The electric moments of the *t*-butyl esters of five different long-chain aliphatic peracids (av. μ = 2.94 ± 0.04 D.) and *t*-butyl perbenzoate (μ = 3.12) have been measured in non-polar solvents at 30°. Like the values for other peroxides, these moments are in accord with a fixed skew configuration about the peroxy grouping, but a more detailed analysis of the results shows that the acyl group probably is twisted somewhat out of its C–O–O plane.

Introduction

Paper I of this series[2] reported the electric moments of some dialkyl peroxides, alkyl hydroperoxides, and diacyl peroxides. The moments were explained by a fixed spatial arrangement of the C–O–O–C group, the azimuthal angle formed by rotating the C–O bonds about the O–O bond being between 100 and 125°. In paper II on peracids[3] the corresponding C–O–O–H azimuthal angle was found to be much less (70°) due to intramolecular hydrogen bonding for which reliable evidence was cited. These conclusions were in agreement with the widely accepted model for hydrogen peroxide proposed by Penney and Sutherland.[4]

More recently, X-ray studies of single crystals of hydrogen peroxide dihydrate[5] and infrared measurements of hydrogen peroxide[6] and of alkyl hydroperoxides[7] have further confirmed that model. The same type of fixed skew arrangement of the C–S–S–C group in disulfides accounts for their dipole moments.[8–10]

Establishment of the Penney–Sutherland structure for the O–O part of the organic peroxide molecules permits more certain interpretation of the dipole moments with respect to other parts of those molecules. For example, one may now consider the rotation of an organic group about the bond attaching it to the peroxy grouping. The *t*-butyl peresters reported here are useful reference substances for such purposes because with them one has to consider only the rotation of the acyl group, rotation of the *t*-butyl group having no effect upon the moment. Treatment of the diacyl peroxides[2]

was complicated by the simultaneous rotation of two groups and with the peracids[3] the effect of acyl group rotation was submerged by the effect of chelation with the OH hydrogen.

This paper presents the first systematic measurement and analysis of the dipole moments of peresters. The values obtained earlier for diacyl peroxides and peracids are reconsidered in view of the findings for the peresters.

Results and Discussion

The results of the measurements are shown in Table I which gives the dipole moments, μ, calculated by the Halverstadt and Kumler[11] method from the dielectric constant, density, and refractive index data. The symbols used in the table are as defined earlier.[2] For the calculated molar refractions, the atomic refraction of the peroxidic oxygen[12] was taken as 2.19 cc. mole^{-1}.

The mean of the moment values for the five aliphatic peresters is 2.94 D. with a mean deviation of ±0.04 D. Structural interpretation of this result can be based upon the diagram
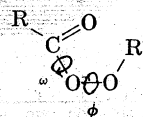
The molecular moment, as a function of the bond moments, bond angles, and azimuthal angles ω and ϕ, will obey the same general formula as developed for the peracids,[3] with H replaced by R′, the *t*-butyl group. In that formula, we assume

planarity for the C–C–O group and measure ω in a clockwise direction looking along the C–O axis from C to O for measurement of rotation of the acyl group out of the plane containing the O–O axis. The other dihedral angle, ϕ, is measured in a clockwise direction looking along the O–O axis from right to left for rotation of the O–O–R′ plane out of the C–O–O plane. The reference diagram shows ω and ϕ both at zero.

If we take the bond angles and bond moments the same as taken earlier for diacyl peroxides,[2] peracids,[3] dialkylperoxides,[2,9] and alkyl hydroperoxides,[2,9] but with the C–O moment equal to 0.73 D. in the acyl group, eq. 1 results.

(1) A report of work done under contract with the U. S. Department of Agriculture and authorized by the Research and Marketing Act of 1946. The contract is supervised by the Eastern Utilization Research Service. This work was presented at the Delaware Valley Regional Meeting of the American Chemical Society, Philadelphia, Pa., January 25, 1962.

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(3) J. R. Rittenhouse, W. Lobunez, D. Swern, and J. G. Miller, *ibid.*, **80**, 4850 (1958).

(4) W. G. Penney and G. B. B. M. Sutherland, *Trans. Faraday Soc.*, **30**, 898 (1934); *J. Chem. Phys.*, **2**, 492 (1934).

(5) I. Olovsson and D. H. Templeton, *Acta Chem. Scand.*, **14**, 1325 (1960).

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(7) M. A. Kovner, A. V. Karyakin, and A. P. Efimov. *Opt. i Spektroskopiya*, **8** (No. 1), 64 (1960).

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(11) I. F. Halverstadt and W. D. Kumler, *J. Am. Chem. Soc.*, **64**, 2988 (1942).

(12) N. Milas, D. M. Surgenor, and L. H. Perry, *ibid.*, **68**, 1617 (1946).

TABLE I

SUMMARY OF THE DILUTE SOLUTION VALUES OF THE DIPOLE MOMENTS OF t-BUTYL PERESTERS AT 30°

| Perester (solvent)	ϵ_{10}	α	V_{10}	β	n^2_{10}	γ	P_{20}	MR_D Obsd.	Theor.	μ
Perpelargonate (benzene)	2.2626	3.8157	1.1520	−0.0218	2.23405	−0.2165	244.27	66.26	66.45	2.98
Perpelargonate (benzene)	2.2626	3.7318	....	......	.....	......	240.57		66.45	2.94
Percaprate (benzene)	2.2624	3.6035	1.1516	− .0113	2.23410	− .1689	249.98	73.33	71.09	2.96
Percaprate (benzene)	2.2630	3.5431	1.1518	− .0145	2.23410	− .1954	246.97	71.80		2.95
Percaprate (benzene)	2.2629	3.5719	1.1521	− .02143	2.23412	− .2050	246.87	70.84		2.96
Perlaurate (benzene)	2.2621	3.0849	1.1520	− .01166	2.23414	− .1967	251.88	80.22	80.30	2.92
Perlaurate (benzene)	2.2640	2.9133	1.1518	− .0158	2.23430	− .2113	242.57	79.12		2.85
Perlaurate (n-hexane)	1.8740	2.1237	1.5364	− .4201	1.87690	.1512	246.30	81.42		2.86
Permyristate (benzene)	2.2628	2.6084	1.1516	− .00294	2.23440	− .1909	251.24	89.56	89.54	2.84
Permyristate (benzene)	2.2628	2.679					255.27			2.87
Permyristate (benzene)	2.2627	2.8238	1.1520	− .00125	2.23445	− .1714	263.80	90.87		2.93
Perpalmitate (benzene)	2.2626	2.6843	1.1519	− .00082	2.23411	− .1616	279.72	99.98	98.77	2.99
Perpalmitate (benzene)	2.2633	2.6896	1.1521	− .0074	2.23390	− .2191	279.44	95.72		3.02
Perpalmitate (benzene)	2.2627	2.6067	1.1520	− .008	2.23411	− .1576	274.21	99.56		2.95
Perpalmitate (n-hexane)	1.8758	1.9479	1.5365	− .4248	1.8767	.1553	278.95	97.84		3.00
Perbenzoate (benzene)	2.2627	5.3317	1.1516	− .1781	2.23438		252.91	55.12	53.24	3.14
Perbenzoate (n-hexane)	1.8716	3.3775	1.5368	− .5764	....	......	243.75			3.09
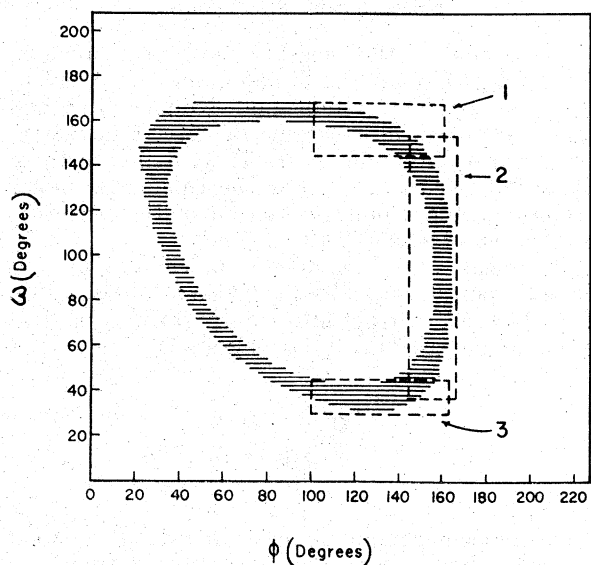
Fig. 1.—Combinations of ω and ϕ for which $\mu = 2.94 \pm 0.04$ D.

$$\mu^2 = (-0.2550 - 0.2550 \cos \phi + 2.2599 \cos \omega)^2 + (2.2599 \sin \omega + 0.9852 \sin \phi)^2 + (0.5208 - 0.9517 \cos \phi)^2 \quad (1)$$

The change from 0.62 to 0.73 for the C–O moment in the acyl group seemed appropriate in view of the experience of others with esters and acids.[13]

Equation 1 gives μ as a function of ϕ and ω and was used to find the simultaneous values of ϕ and ω which correspond to the observed value of μ, i.e., 2.94 ± 0.04. A Univac 90 solid state computer was readily programmed for aid in these calculations. The results are shown in Fig. 1 for 2° ω intervals. Omitted from the figure is the equivalent set of ω–ϕ solutions which would have been obtained by taking the mirror-images of the set shown.

(13) C. P. Smyth, "Dielectric Behavior and Structure," McGraw-Hill Book Co., Inc., New York, N. Y., 1955, p. 306.

For the aliphatic peresters, the Penney–Sutherland model and also steric hindrance, as observed with Fisher–Taylor–Hirschfelder models, eliminate the structures in which ϕ is less than 100°. The remaining structures are put in three groups indicated in Fig. 1 by the areas 1, 2, and 3. Each of these three areas may be regarded as representing a single structure undergoing simultaneous change of ϕ and ω within depicted limits, i.e., a librating molecule. Thus, for area 1, defined by $\phi = 100$–160°, $\omega = 140$–165°, we would have the librating molecule of average moment $\bar{\mu}$, given by the following equation which assumes equal probabilities of all the forms encompassed by its limits

$$(\bar{\mu})^2 = \int_{100}^{160} \int_{140}^{165} \mu^2 d\omega d\phi \bigg/ \int_{100}^{160} \int_{140}^{165} d\omega d\phi$$

This average moment is found to be 2.97 D., showing the validity of this interpretation. Similarly, area 2, with $\phi = 145$–165° and $\omega = 30$–150°, gives $\bar{\mu} = 2.93$, and area 3, with $\phi = 100$–150° and $\omega = 30$–45°, has $\bar{\mu} = 2.93$.

Of these three structures, we may dismiss the second one on two counts. First, the mean value of ϕ about which the vibrations take place, 155°, seems much too large compared to the values found for other peroxides. Second, the range of ω values, 30–150°, is highly improbable in view of the resonance expected for peresters.
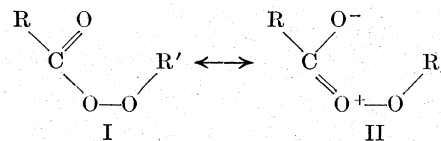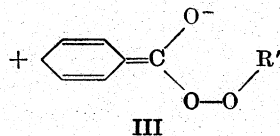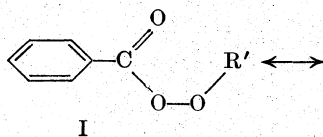

Such resonance would call for ω values near 0 or 180°, due to the double bond character it gives to the C–O link. In ordinary carboxylic acids and their esters this resonance is large, contributions of form II causing a shortening of the C–O bond length[14] from its normal value, 1.46 ± 0.04 Å., to 1.36 ± 0.04 Å. Resonance energies due to

(14) P. W. Allen and L. E. Sutton, Acta Cryst., 3, 346 (1950).

the same contributions are approximately 30, 15, and 20 kcal. mole^{-1} for anhydrides, acids, and esters, as determined from heats of combustion.[15] The persistence of this resonance in going to the peroxide analogs is shown by the infrared absorption maxima due to the C=O and C–O stretching frequencies. This has been demonstrated for esters and peresters,[16,17] acids and peracids,[18] and anhydrides and diacyl peroxides.[16,19]

Such resonance would involve overlap of the p orbital of the acyl carbon atom with the p orbital of the adjacent peroxy-oxygen atom. Although the resonance energy will be at a maximum when the acyl group is completely coplanar with the C–O–O group, i.e., when ω is 0 or 180°, such perfect coplanarity is not required for the resonance to exist. Dewar[20] has shown that the resonance energy will vary as cos ω or cos^2 ω. While this would eliminate the second structure, it would make the other two plausible. The cause of the twisting of the acyl group out of the C–O–O plane is not evident, although it may be due to electrostatic interaction of the carbonyl and t-butoxyl dipoles attended by effects due to the size of the alkyl groups. While librations about higher values of ω (140–165°) would meet lower repulsion between those dipoles, the long alkyl chains (R) would meet steric interference with the t-butyl group. For this reason, we favor the structure in which the oscillating twist is centered about values of ω in the neighborhood of 35°. In general, dipole moment values indicate that in ordinary esters the carbonyl and alkoxyl groups are cis to each other.[21] It also is interesting that electron diffraction studies[13,14] have shown ω values of 25–40° for methyl formate and methyl acetate.

We may now consider the moment of t-butyl perbenzoate. That moment, 3.12 ± 0.04 D., is accounted for by adding to the bond moments of the aliphatic peresters a resonance moment due to contributions from an additional resonance form that exists for t-butyl perbenzoate

I

III

When this additional moment is taken equal to

0.4 D. and located along the line of centers of the carbonyl oxygen atom and the benzene ring, with its negative end toward the oxygen atom, then the molecular moment is given by the same combinations of ϕ and ω as shown in Fig. 1. The existence of such a resonance moment also is apparent in ethyl benzoate,[22] which has a dipole moment about 0.15 D. higher than the ethyl esters of the saturated aliphatic carboxylic acids. Furthermore, the molar refractions (Table II) of the pure substances[23] show that optical exaltation in t-butyl perbenzoate is markedly higher than in the aliphatic peresters. This also can be explained in terms of enhanced delocalization, indicated by structure III.

TABLE II

THE MOLAR REFRACTION OF t-BUTYL PERESTERS MEASURED FOR THE PURE LIQUIDS[23]

| | | MR_D | |
Perester	Obsd.	Calcd.	Exaltation
Perpelargonate	66.70	66.45	0.25
Percaprate	71.37	71.09	.28
Perlaurate	80.65	80.30	.35
Permyristate	89.96	89.54	.42
Perbenzoate	54.86	53.24	1.62
Perbenzoate[12]	54.84	53.24	1.60

In summary, the dipole moment values for all of the t-butyl peresters studied here indicate that those esters have the Penney–Sutherland structure with restricted oscillation of the acyl groups out of plane with the peroxy grouping.

Following this analysis of the data for the peresters, the dipole moment values already published[2,3,9] for alkyl peroxides, alkyl hydroperoxides, peracids, and diacyl peroxides were treated in the same detailed manner. No essential change resulted from these analyses. It should be noted, however, that in the peracids and diacyl peroxides oscillations of the acyl groups from strict coplanarity with the peroxy oxygen atoms are indicated. Concerning the diacyl peroxides, the interesting earlier finding[2] of opposition of the carbonyl group directions was confirmed. Bellamy and his coworkers[19] recently have come to the same conclusion from consideration of the relative intensities of the infrared absorption doublets caused by the carbonyl groups of the diacyl peroxides.

Experimental

Preparation of Materials.—The t-butyl peresters were prepared by the pyridine acylation method of Silbert and Swern.[23] Important characterizing physical and chemical data of the substances involved are given in Table III. Included are the properties of peresters generously supplied by Dr. Leonard S. Silbert of the Eastern Utilization Research and Development Division, U. S. Department of Agriculture. The acyl halides were obtained from acids prepared by hydrolysis of the purified methyl esters. The methyl esters were analyzed for purity by gas chromatography in which 5-μl. samples were passed through a 6.1-ft. column of 25% silicone oil on Chromosorb maintained at 210° at a flow rate at 120 cc. min.$^{-1}$. There resulted single peaks, indicating the absence of homologs. Of the three different methods of final purification, molecular distillation in a short-path still and passage through a column of activated

(15) G. W. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1955, pp. 99–100.

(16) W. H. T. Davison, J. Chem. Soc., 2456 (1951).

(17) Private communication from Dr. Leonard S. Silbert.

(18) M. Davies and O. Thomas, Discussions Faraday Soc., 9, 335 (1950).

(19) L. J. Bellamy, B. R. Connelly, A. R. Philpotts, and R. L. Williams, Z. Elektrochem., 64, 563 (1960).

(20) M. J. S. Dewar, J. Am. Chem. Soc., 74, 3349 (1952); see also, L. L. Ingraham in "Steric Effects in Organic Chemistry," M. S. Newman, ed., John Wiley and Sons, Inc., New York, N. Y., 1956, pp. 479–522.

(21) G. W. Wheland, ref. 15, p. 235; R. J. B. Marsden and L. E. Sutton, J. Chem. Soc., 1383 (1936).

(22) C. S. Copeland and M. W. Rigg, J. Am. Chem. Soc., 73, 3584 (1951).

(23) L. S. Silbert and D. Swern, ibid., 81, 2364 (1959). The first row of data for t-butyl perbenzoate in Table II were kindly determined for us by Dr. Silbert.

Table III

CHARACTERIZING PROPERTIES OF THE t-BUTYL PERESTERS AND INTERMEDIATES IN THEIR PREPARATION

Acyl group	Methyl ester B.p., °C. (mm.)	n^{25}D	Acyl chloride B.p., °C. (mm.)	Recrystn. temp., °C.	Final method of purificn.	t-Butyl perester n^{30}D	$d^{30}{}_4$	Available oxygen (% of theor.)
Lauric	139–141 (15)	1.4301	145 (18)	−40	Recryst.	1.4333	0.8783	99.7
Lauric^a	....	...	....	..	Recryst.	1.4337	.8784	99.5
Pelargonic^b	....	....	......	30–32^c	Distill.	1.4273	.8868	99.7
Capric	114 (15)	1.4235	53 (1.5)	−45	Florisil, alumina	1.4297	.8832	99.7
Capric^a	....	....	......	..	Recryst.	1.4293	.8833	100.3
Myristic	153–155 (10)	1.4346	144 (1.5)	−45	Recryst.	1.4373	.8752	100.0
Myristic^a	....	....	......	..	Recryst.	1.4368	.8751	100.0
Palmitic	194 (12)	1.4355 (n^{35}D)	137 (0.3)	−45	Recryst.	....	....	99.6
Palmitic	....	...	......	..	Florisil, alumina	....	....	99.2
Benzoic^d	....	....	39.5 (17)	−45	Recryst.	1.4957	1.00337	99.2

^{a} Perester supplied by Dr. L. S. Silbert. ^{b} Pelargonyl chloride supplied by Dr. L. S. Silbert. ^{c} Boiling point of perester at 10 μ. ^{d} N.B.S. benzoic acid was used.

alumina and "Florisil" ensured removal of water which might have occluded during recrystallization. The dipole moments of these samples agreed with the values for those obtained by recrystallization, indicating the absence of water in all the samples. Available oxygen was determined by the improved iodometric method of Silbert and Swern.[24]

Benzene.—Thiophene-free C.P. benzene was dried over phosphorus pentoxide for several days and distilled through a 1.5 × 130 cm. cylindrical column packed with 3/8 in. glass helices, then stored over Drierite until used. All transfers of solvent for weighing and washing were made using drying tubes to avoid contamination by atmospheric moisture.

n-Hexane.—Phillips pure n-hexane was treated with concentrated sulfuric acid for 7 days and was then washed with water and 5% sodium carbonate solution. It finally was distilled over phosphorus pentoxide and stored in the same manner as the benzene.

Petroleum Ether.—Low boiling, olefin-free petroleum ether, used as solvent in the preparation of the peresters, was prepared in the same manner as was n-hexane.

t-Butyl Hydroperoxide.—The t-butyl hydroperoxide was prepared as described earlier.[2] The fraction boiling at 42.5° at 18 mm. was used in the preparation of the peresters.

Apparatus and Methods.—Dielectric constants, refractive indices, and densities were measured as described earlier,[2,3] but for most of the capacitance measurements a General Radio Company 716 CS 1 radiofrequency bridge, 1330 A oscillator, and 1212 A null-detector were employed. Solute weight fractions were in the range 0.001 to 0.012. Temperatures were maintained at 30.00 ± 0.005°.

(24) L. S. Silbert and D. Swern, *Anal. Chem.*, **30**, 385 (1958).